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High Purity Nickel/Vanadium Sputtering Components; and Methods of Making Sputtering Components

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HIGH PURITY NICKEL/VANADIUM SPUTTERING COMPONENTS; AND METHODS OF MAKING SPUTTERING COMPONENTS

RELATED PATENT DATA

[0001] This patent is related to U.S. Provisional Patent Application Serial No. 60/432,166, which was filed on December 9, 2002.

TECHNICAL FIELD

[0002] The invention relates to high purity nickel/vanadium sputtering components (such as sputtering targets). The invention also relates to methods of making sputtering components.

BACKGROUND OF THE INVENTION

[0003] Nickel/vanadium materials have numerous applications in the semiconductor industry. For instance, the materials can be used in barrier/adhesion layers for under-bump metals to support flip chips, or in C4 (collapsed, controlled, chip connection) assemblies. A typical nickel/vanadium composition is Ni-7V (i.e., a composition containing about 7 weight percent vanadium and the remainder nickel).

[0004] A typical method of forming nickel/vanadium layers in semiconductor processing is physical vapor deposition (PVD). Specifically, the layers are sputter-deposited from a sputtering target. The standard purity for conventional Ni-7V sputtering targets is 3N5 – 3N8 pure (i.e., 99.95% pure to 99.98% pure, by weight, excluding gases). The purity is typically determined by glow discharge

mass spectroscopy (GDMS) and/or LECO® (conductometric) methods, (LECO® is a Registered Trademark of LECO Corporation). The average grain size of conventional Ni-7V sputtering targets is quite large (typically, greater than 50 microns).

[0005] The purity and grain size of the sputtering targets limits the quality of the sputter-deposited materials formed from the targets. Higher purity targets can lead to higher purity sputter-deposited materials, which are desired. Lower average grain sizes in the targets can lead to better physical and/or chemical homogeneity of sputter-deposited materials, which is also desired. Accordingly, it is desired to develop an improved Ni-V sputtering target having higher purity and smaller average grain size.

[0006] A limitation on the purity of conventional nickel/vanadium materials is typically imposed by the purity of vanadium. The nickel/vanadium materials are formed by mixing high purity nickel with high purity vanadium. The nickel can have a purity of 4N5 (99.995 wt%, excluding gases), or even 5N (99.999 wt%, excluding gases), but the vanadium will generally have a purity of 2N5 (99.5 wt%, excluding gases) or lower. The purity of available vanadium thus limits the purity of Ni-V alloys that can be formed. Accordingly, there is a desire to develop improved purity vanadium materials.

[0007] An exemplary prior art physical vapor deposition operation is described with reference to a sputtering apparatus 110 in Fig. 1 to illustrate exemplary components of a sputtering assembly. Apparatus 110 is an example of an ion metal plasma (IMP) apparatus, and comprises a chamber 112 having

sidewalls 114. Chamber 112 is typically a high vacuum chamber. A target construction 10 is provided in an upper region of the chamber, and a substrate 118 is provided in a lower region of the chamber. Substrate 118 is retained on a holder 120, which typically comprises an electrostatic chuck. Target construction 10 would be retained with suitable supporting members (not shown), which can include a power source. An upper shield (not shown) can be provided to shield edges of the target construction 10.

[0008] Substrate 118 can comprise, for example, a semiconductor wafer, such as, for example, a single crystal silicon wafer. A nickel/vanadium film can be over a surface of the substrate in particular utilizations of apparatus 110. Target construction 10 can thus comprise a nickel/vanadium target.

[0009] Material 122 is sputtered from a surface of the target of construction 10 and directed toward substrate 118.

[0010] Generally, the sputtered material will leave the target surface in a number of different directions. This can be problematic, and it is preferred that the sputtered material be directed relatively orthogonally to an upper surface of substrate 118. Accordingly, a focusing coil 126 is provided within chamber 112. The focusing coil can improve the orientation of sputtered materials 122, and is shown directing the sputtered materials relatively orthogonally to the upper surface of substrate 118.

[0011] Coil 126 is retained within chamber 112 by pins 128 which are shown extending through sidewalls of the coil and also through sidewalls 114 of chamber 112. Pins 128 are retained with retaining screws 132 in the shown

configuration. The schematic illustration of Fig. 1 shows heads 130 of the pins along an interior surface of coil 126, and another set of heads 132 of the retaining screws along the exterior surface of chamber sidewalls 114.

[0012] Spacers 140 (which are frequently referred to as cups) extend around pins 128, and are utilized to space coil 126 from sidewalls 114.

[0013] The apparatus shown in Fig. 1 is but one of the many types of PVD apparatuses. Other exemplary apparatuses include apparatuses marketed as or by Unaxis, Balzers, Nexx, Ulvac, Annelva, and NOVELLUS. Some of the apparatuses utilize round sputtering targets, while others utilize other target shapes, such as square and rectangular designs.

SUMMARY OF THE INVENTION

[0014] In one aspect, the invention relates to sputtering components, such as sputtering targets, comprising high-purity Ni-V. The sputtering components can have a small average grain size, with an exemplary average grain size being less than or equal to 40 microns.

[0015] In one aspect, the invention includes methods of making high-purity Ni-V structures.

BRIEF DESCRIPTION OF THE DRAWINGS

[0016] Preferred embodiments of the invention are described below with reference to the following accompanying drawings.

[0017] Fig. 1 is a diagrammatic, cross-sectional view of a prior art physical vapor deposition apparatus shown during a physical vapor deposition (e.g., sputtering) process.

[0018] Fig. 2 is a diagrammatic, cross-sectional view of an exemplary target/backing plate construction of the present invention.

[0019] Fig. 3 is a top view of the Fig. 2 construction, with the cross-section of Fig. 2 extending along the line 2-2 of Fig. 3.

[0020] Fig. 4 is a diagrammatic, cross-sectional view of an exemplary monolithic target construction of the present invention.

[0021] Fig. 5 is a top view of the Fig. 4 construction, with the cross-section of Fig. 4 extending along the line 4-4 of Fig. 5.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0022] This disclosure of the invention is submitted in furtherance of the constitutional purposes of the U.S. Patent Laws "to promote the progress of science and useful arts" (Article 1, Section 8).

[0023] In some aspects, the present invention relates to sputtering components. For purposes of interpreting this disclosure and the claims that follow, the term "sputtering component" refers to any component from which material is sputtered or otherwise removed from during a physical vapor

deposition process. The common sputtering component is a sputtering target, but it is to be understood that sputtering can occur from surfaces of other components besides a sputtering target (such as, for example, coils, pins or cups), during physical vapor deposition. The phrase “sputtered component” refers to a sputtering component from which material has been sputtered or otherwise removed. As will be understood by persons of ordinary skill in the art, sputtering targets can be formed from metal blanks, plates or slabs. The phrase "sputtering target pre-fab" is utilized herein to refer to metal blanks, plates, slabs etc. that will be further processed into sputtering targets, and the phrase "sputtering target structure" is utilized to generically encompass sputtering targets themselves and sputtering target pre-fabs. A "sputtering component pre-fab" is to be understood to refer to metal blanks, plates, slabs, etc., utilized to form sputtering components; and the phrase "sputtering component structure" is to be understood to encompass sputtering component pre-fabs as well as the finished components. Sputtering targets encompassed by various of the aspects of the present invention can have any suitable geometry, and can be either bonded assemblies or monolithic sputtering targets. Sputtering targets encompassed by various of the aspects of the present invention can be configured for utilization in any suitable apparatus, including, but not limited to, the apparatuses described in the "Background" section of this disclosure.

[0024] In some aspects, structures of the present invention have particular average grain sizes. The phrase “average grain size” as used herein means an average grain size which has been determined by standard methods known to

those skilled in the art. Average grain size was determined for the exemplary compositions described herein by the ASTM E112 Standard Test Method for Determining Average Grain Size. Particular structures of the present invention can have an average grain size throughout an entirety of the structures of less than or equal to around 40 microns, preferably less than or equal to around 30 microns, and more preferably less than or equal to around 20 microns. The conversion between micron grain size and ASTM grain size number is described in Table 1 for some exemplary grain sizes.

Table 1

Micron Grain Size	ASTM Grain Size Number
Less than or equal to around 40	Greater than or equal to around 6.3
Less than or equal to around 30	Greater than or equal to around 7.2
Less than or equal to around 20	Greater than or equal to around 8.3

[0025] In some aspects, the invention includes methodology for making high purity vanadium compositions. Exemplary methodology includes molten salt electrolysis. The salt can be an alkali-halogen salt, such as, for example, NaCl. The electrolysis can be repeated multiple, sequential times to obtain a desired purity of vanadium. In particular aspects of the invention, the composition resulting from the electrolysis can be at least 99.995 weight%, excluding gases, pure in vanadium, or even at least 99.999 weight%, excluding gases, pure in vanadium.

[0026] In some aspects, the invention includes methods of producing high-purity nickel/vanadium sputtering components. Raw materials of high purity

nickel and vanadium are provided. The nickel raw material will preferably have an overall purity of at least 99.995 weight%, excluding gases, and more preferably at least 99.999 weight%, excluding gases. The vanadium raw material will have an overall purity of at least 99.9 weight%, excluding gases; more preferably at least 99.995 weight%, excluding gases; and even more preferably at least 99.999 weight%, excluding gases. The nickel and vanadium raw materials are melted together to form a molten alloy comprising the nickel and vanadium. The specific composition of the desired alloy will dictate the amount of each raw material that is incorporated into the molten alloy. The molten alloy can then be cooled to form a nickel/vanadium structure which is at least 99.99%, 99.995%, or 99.999% pure in nickel and vanadium (by weight, excluding gases).

[0027] The structure formed from the alloy can be a sputtering component pre-fab (such as, for example, a sputtering target pre-fab) or a sputtering component.

[0028] In particular aspects, a molten nickel/vanadium alloy is cast into a high-purity nickel-vanadium ingot using appropriate conventional vacuum melting techniques, such as, for example, electron-beam, vacuum induction melting (VIM) or vacuum arc remelting (VAR). Repeated vacuum melting steps can be employed as desired to improve the overall purity of the ingot and/or to obtain a resulting high-purity nickel/vanadium alloy with a homogenous composition. The resulting high-purity Ni-V ingot can be any desired shape (i.e., rectangular, square, round, etc.), and can be any desired size.

[0029] The high-purity Ni-V ingot can be subjected to thermo-mechanical processing in order to apply deformation and annealing into the metal of the ingot to impart a desired grain size within metal. Exemplary thermo-mechanical processing can utilize a series of hot rolling steps and cold rolling steps (preferably with all of the rolling steps comprising rolling along the same direction as one another) in combination with annealing. A nickel/vanadium structure resulting from the thermo-mechanical processing can be a nickel/vanadium plate or blank. Such structure can be a target suitable for bonding to a backing plate, or can be a target pre-fab suitable for appropriate machining to form a target structure which can be bonded to a backing plate. Alternatively, the nickel/vanadium structure can be a monolithic target or a target pre-fab suitable for appropriate machining to form the structure into a monolithic target. An exemplary thermo-mechanical processing sequence is provided in an example immediately before the claims.

[0030] Nickel/vanadium alloys and structures formed in accordance with methodology of the present invention can have an overall metallic purity of nickel/vanadium of at least 99.99%, by weight, excluding gases; at least 99.995% (by weight, excluding gases); or even at least 99.999% (by weight, excluding gases). In determining the overall metallic purity of the nickel/vanadium compositions, all detectable impurities are totaled (elements at or below the detection limit are not included). The standard analytical techniques for determining purity are GDMS and LECO®. The standard alloy composition in the industry today is Ni-7V. However, it is to be understood that

the sputtering components described herein may comprise a different amount of vanadium (i.e., more or less than 7 weight percent). Typically, a nickel/vanadium alloy of the present invention will comprise from about 4 weight percent vanadium (with the rest of the alloy being nickel) to about 10 weight percent vanadium (with the rest of the alloy being nickel). Results of an analysis of a nickel/vanadium alloy formed in accordance with an aspect of the present invention are presented in Table 2. The alloy comprises 6.64 weight percent vanadium.

Table 2

Element	Ppm	Method	Element	ppm	Method
Li	< 0.001	GDMS	Ta	< 1	GDMS
B	0.1	GDMS	W	0.61	GDMS
F	<0.01	GDMS	Pb	0.3	GDMS
Na	0.04	GDMS	Bi	< 0.005	GDMS
Mg	0.37	GDMS	Th	< 0.001	GDMS
Al	14	GDMS	U	0.001	GDMS
Si	17	GDMS	C	27	LECO
P	0.91	GDMS	N	28	LECO
S	< 10	LECO	O	160	LECO
Cl	0.12	GDMS			
K	< 0.01	GDMS			
Ca	< 0.05	GDMS			
Ti	2.4	GDMS			
Cr	5.2	GDMS			
Mn	6.4	GDMS			
Fe	27	GDMS			
Co	2.7	GDMS			
Cu	11	GDMS			
Zn	0.14	GDMS			
Zr	2.3	GDMS			
Nb	1.3	GDMS			
Mo	4.4	GDMS			
Hf	0.03	GDMS			

[0031] An exemplary target construction 11 which can be formed in accordance with methodology of the present invention is described with reference to Figs. 2 and 3. The construction comprises a backing plate 12, a target 14, and a bond 16 between the target and backing plate. The bond can be a diffusion bond, or can comprise an interlayer material (such as, for example, a solder). The target 14 can comprise high purity nickel/vanadium in accordance with various aspects of the present invention. The construction 11 can be utilized as the target construction 10 in a deposition apparatus of the type described above with reference to Fig. 1.

[0032] Another exemplary target construction 20 which can be formed in accordance with methodology of the present invention is described with reference to Figs. 4 and 5. The construction comprises a monolithic target 22. The target 22 can comprise high purity nickel/vanadium in accordance with various aspects of the present invention. The construction 20 can be utilized as the target 10 in a deposition apparatus of the type described above with reference to Fig. 1.

[0033] Any components within a sputtering chamber (such as the chamber of Fig. 1) that are exposed to sputtering conditions can release some material. Accordingly, components besides the target can, in some applications, be considered sputtering components. The items within a chamber that can be sputtering components, include, but are not limited to, coils, cover rings, clamps, shields, pins and cups. It some applications, it can be problematic if materials sputter from non-target sputtering components in that the materials sputtered

from the non-target components can contaminate materials sputtered from the target. The problem can be alleviated, and even prevented, if all sputtering components and potential sputtering components within a reaction chamber are formed from the same material as the target. Accordingly, it can be desired to form the target and one or more non-target sputtering components (such as, for example, one or more of coils, cover rings, clamps, shields, pins, cups, etc.) from high purity nickel/vanadium in various aspects of the invention.

Nickel/vanadium sputtering components formed in accordance with the present invention can be utilized for deposition of Ni-V layers over semiconductor substrates. The Ni-V layers can be utilized in under-bump and C4 technologies. Additionally, layers formed from high purity, small grain-size Ni-V sputtering targets can be used for other semiconductor applications besides under-bump and C4 assemblies. For instance, the layers can be utilized for silicide formation and high-end coatings in semiconductor applications. Nickel has been investigated for use in silicide and high-end coatings of semiconductor applications, but the magnetic properties of nickel render pure nickel unsuitable for many of such applications. Addition of vanadium to nickel forms an alloy having suitable magnetic properties for semiconductor applications, which is a reason that Ni-7V is utilized in various applications. However, conventional nickel/vanadium alloys have too low of a purity to be suitable for silicide and high-end coatings. In contrast, the relatively pure Ni-V alloys that can be produced from sputtering targets of the present invention can be suitable for silicide and high-end coatings applications.

EXAMPLE

[0034] A high-purity Ni-V ingot is uni-directionally hot-rolled at a high temperature (such as a temperature from 1400°F to 2400°F (760°C – 1316°C)) to decrease a thickness of the ingot and produce a slab (the thickness of the slab can be, for example, about 1.5" (3.81 cm)); with a typical deformation induced by the hot rolling being at least about 90% (i.e, the thickness of the slab is less than or equal to about 10% of the starting thickness of the ingot). The slab is cooled to room temperature and cut into several smaller sections. The sections are subjected to hot-rolling (at, for example, a temperature of from 1400°F to 2400°F), followed by cold-rolling (at for example, about room temperature) to reduce the thickness of the sections to a final thickness (for example about 0.35" (0.89 cm)). The hot and cold rolling across the sections is preferably uni-directional, and along the same direction as the uni-directional rolling across the ingot. After the hot and cold rolling of the sections, the sections are annealed at an increased temperature (for example, about 1600°F (871 °C) for about 1 hour).